Time-gated electroluminescence spectroscopy of polymer light-emitting diodes as a probe of carrier dynamics and trapping

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We present time-gated electroluminescence (EL) spectroscopy of a polyfluorene-based conjugated polymer. The technique is shown to be sensitive enough to pick out impurity emission orders of magnitude weaker than the cw emission. By considering the temperature dependence of the delayed emission spectra and also the dependence on a constant-bias offset it is shown that both geminate pair formation and carrier trapping during operation result in a long EL decay tail. The technique also provides a direct probe of the validity of the Einstein law in conjugated polymers. The diffusion mobility is found to exceed the drift mobility by a factor of 12.

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Conjugated polymers have opened up a whole array of device and material physics, with fundamentally different properties to conventional crystalline inorganic semiconductors. They have been used in a wide range of optoelectronic applications, such as light-emitting diodes (LED's) and lasers. Much effort has been devoted to the understanding of charge transport in these materials. Considerable attention has been paid to the dynamic response of polymer LED's,[1–3] which is both of importance for the design of passively addressed matrix displays and for feasibility studies of electrically driven polymer based laser diodes. To date, most of the investigations into the transient response of LED's have focused on spectrally integrated studies. However, gated fluorescence spectroscopy has been found to be a powerful tool for investigating the role of optically generated charge carriers in the delayed emission from polymers,[4] yet has to our knowledge not previously been used to extract comparable information from electroluminescent devices. In the case of LED's the situation of delayed emission due to charge carriers is particularly interesting as charge carrier traps are filled during operation. Gated electroluminescence (EL) detection can hence provide a spectroscopic means of trap characterization.

In this paper we present microsecond-gated EL spectroscopy of the delayed emission from a polyfluorene-containing LED after termination of the driving voltage pulse. Polyfluorenes are a promising class of materials for efficient blue LED's.[5–9] However, in many cases the emission is accompanied by a broad green band, which has been assigned to either defect[6,7] or excimer emission.[8,9] In order to obtain a well-defined delayed emission signal, a small concentration of a phosphorescent platinum porphyrin emitter was added, which provides a long-lived luminescence signal. Such blend systems are currently of great interest due to the possibility of triplet harvesting.[5,10] However, in the case of polyfluorene-porphyrin blends it has been argued that direct recombination by hole trapping on the porphyrin dominates over triplet energy transfer.[5] The delayed emission spectra are found to exhibit a range of dynamical processes, which are totally masked in the cw operation. Using gated EL, we are able to argue in favor of preferential recombination on defect sites due to charge trapping.

Single-layer LED's were fabricated on solution-etched indium tin oxide (ITO) substrates ultrasonicated in isopropanol. A charge transport layer (50 nm) of poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate was deposited on the ITO layers and dried on a hot plate. Solutions of the polyfluorene derivative poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PF2/6) doped with approximately 0.001% by weight of the phosphorescent dye 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum (II) (PtOEP) were spin coated onto the substrates to yield films typically 100 nm thick, which were then contacted with 15-nm-thick calcium electrodes, 4 mm^2 in area, capped by an aluminum layer (150 nm). The samples were mounted in a water-cooled cold finger cryostat under rotary pump vacuum. Figure 1 shows the EL spectrum of a typical device under cw operation with the structures of PF2/6 and PtOEP inset. The spectra were detected by an EG&G intensified red-enhanced gated diode array coupled to a 0.3-m monochromator with a grating of 150 lines/mm. Two main bands are observed: one in the green and the other in the blue with vibronic peaks at 420, 440, and 475 nm. The blue feature is associated with emission from the PF2/6 singlet exciton. The broad green emission band centered at 525 nm has previously been attributed to emission from an excimer,[8,9] although it has also been pointed out that the position and shape of the emission band are identical to that of fluorenone,[6,7] which may be formed on the polymer backbone by oxidation. It is hence also conceivable that the broad green band originates from a chemical defect site, which could act as a trap for charge

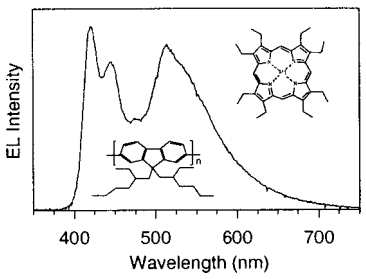

FIG. 1. cw EL spectrum of a single-layer polyfluorene LED. The insets show the structures of PF2/6 and PtOEP.

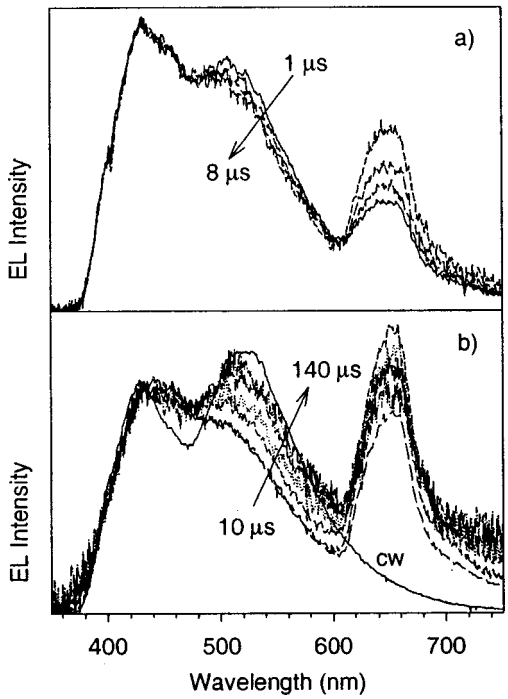

FIG. 2. Delayed EL spectra recorded through a slit corresponding to a spectral resolution of 10 nm after turnoff of a 40-μs 5-V pulse. (a) Spectra recorded with 4-μs time windows at delays of 1, 2, 4, and 8 μs. (b) Spectra recorded with 40-μs time windows at delays of 10, 30, 50, 80, 100, and 140 μs. The solid line shows the cw spectrum measured under the same conditions.

carriers.[6] The observation of the green band in photoluminescence measurements on dilute solutions also supports this notion.[11] The delayed EL spectra suggest that charge carrier trapping plays an important role and that the two bands result from different emitting species. Figure 2(a) shows the EL spectra recorded in 4-μs windows between 1 and 8 μs after termination of a 5-V voltage pulse (corresponding to a current density of approximately 25 mA cm^{-2}) of 40 μs length. The spectra appear broadened in comparison to Fig. 1 as the entrance slit was widened, resulting in a spectral resolution of 10 nm. In contrast to the cw emission spectrum, emission from the PtOEP guest molecules is clearly seen, peaking at 650 nm. The spectra are normalized to the blue singlet emission band. Shortly after the voltage turnoff the green band is found to decrease in intensity with respect to the blue band. Figure 2(b) shows the temporal evolution of the delayed EL spectra recorded in 40-μs windows between 10 and 140 μs after the end of the voltage pulse. For comparison, the cw spectrum is also plotted. Beyond 10 μs after turnoff the green band is found to rise again with respect to the blue band and approaches the emission ratio of the new cw spectrum at 140 μs, demonstrating that the two polyfluorene emission components observed in cw and gated detection are identical.

The temporal evolution of the delayed PtOEP and PF2/6 emission intensity is shown in Fig. 3. In contrast to spectrally integrated transient EL, the gated spectroscopy technique is able to precisely differentiate between two entirely different emitting species. The low-concentration phosphorescent

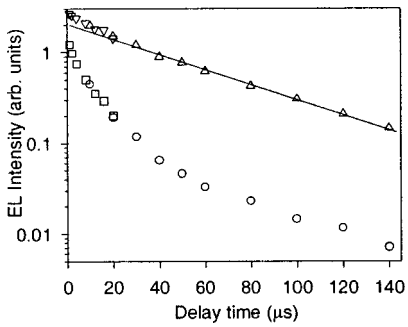

FIG. 3. Temporal decay of the 650-nm peak and the blue emission peak. ▽: 4-μs gate, PtOEP emission. △: 40-μs gate, PtOEP emission. □: 4-μs gate, PF2/6 emission. ○: 40-μs gate, PF2/6 emission.

guest emission decays virtually singly exponentially with a lifetime of 51 μs, which compares to previous measurements.[5] At times below 10 μs a small deviation is observed, which is believed to be due to delayed hole capture on the molecules, leading to a quenching of the excited state. As the lifetime of singlet excitons on the host is shorter than 1 ns, the delayed host recombination has to be due to delayed charge recombination, in contrast to the delayed guest emission, which is due to phosphorescence. The host emission decays nonexponentially by over two orders of magnitude between 1 and 140 μs after the voltage turnoff.

The observation that the blue to green emission ratio changes with delay time after device turnoff suggests that different trapping and recombination processes give rise to the delayed emission from the two bands. Figure 4 shows the temperature dependence of the change in green to blue emission ratio with time. The green band is found to increase more strongly with time as the temperature is raised, indicating a thermal activation of the delayed recombination mechanism. In order to probe the origin of the delayed emission spectra in LED's, a constant-bias offset was applied to the voltage pulse. For a negative-bias offset between 0 and -2.4 V no change in the delayed emission spectrum 20 μs after voltage turnoff was observed. However, as can be seen in Fig. 5, even a very small positive-bias offset dramatically modifies the delayed emission spectrum, leading to an overall increase in delayed emission. It should be noted at this point that the applied bias offsets are significantly smaller than the bias for EL turnon (approximately 3 V). As the bias

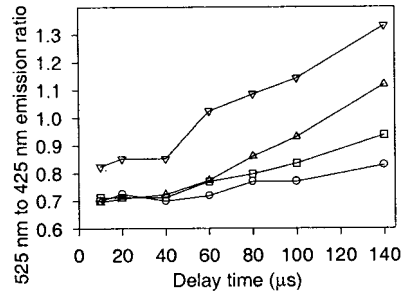

FIG. 4. Evolution of the 525-nm to 425-nm peak emission ratio detected with a 40-μs gate as a function of time for different temperatures: 263 K (○), 283 K (□), 303 K (△) and 323 K (▽).

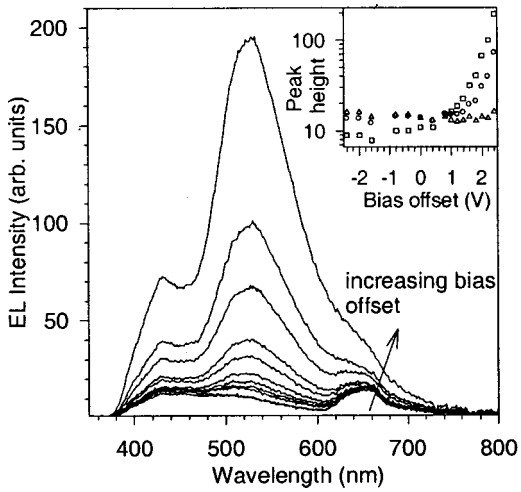

FIG. 5. Change of the delayed EL intensity 20 μs after the end of the voltage pulse with constant-bias offset, detected with a 40-μs gate. The inset shows the three peak intensities [430 nm (○), 525 nm (□), and 650 nm (△)] as a function of bias offset. The voltage pulse amplitude was kept constant at 5 V.

offset is increased, the shape of the delayed spectrum changes and the emission contribution from the green band increases more strongly than the blue emission. As shown in the inset, the functional dependences of the peak heights of the green and blue bands on bias offset are similar and vary superlinearly with bias offset. The PtOEP delayed guest emission is unaffected by the bias offset.

The delayed emission results from recombination of trapped and mobile carriers. As the bias offset is changed, the field and hence the carrier distribution inside the device post switchoff are altered. To a first approximation the device acts as a parallel plate capacitor. After turnoff the internal field is reversed and carriers within the device are sucked back to the electrodes they emanated from. As a reverse-bias offset does not alter the delayed recombination spectra, it is concluded that mobile carriers are rapidly swept out of the device by the built-in field and that the delayed recombination results through recombination of both trapped electrons and holes or of tightly geminately bound carriers, whose own Coulombic field is stronger than the applied external field. As the bias offset is increased, both the blue and green delayed emissions are enhanced. The depletion of the device of mobile carriers becomes less efficient, and as a result, recombination can occur with trapped carriers. As the delayed PtOEP emission intensity does not depend on bias offset, it can also be concluded that the PtOEP molecules are excited during the voltage pulse and not, like the host polymer, post switchoff by delayed recombination.

The observation of nondispersive hole transport in time-of-flight measurements on polyfluorenes has previously been invoked as an argument for a high degree of structural and chemical purity in these materials as well as the absence of charge trapping states.[12] However, the fact that electron photocurrent transients on the same material exhibit dispersive transport suggests a small yet significant contribution from electron trapping states. As the bias offset is increased, mobile carriers recombine with trapped carriers of the opposite

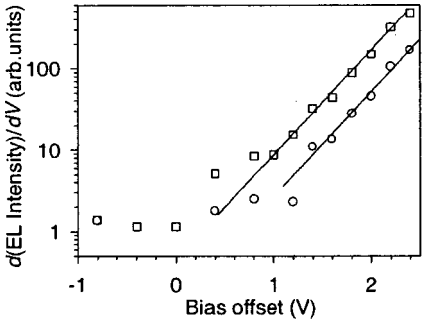

FIG. 6. First derivative of the peak intensity data from Fig. 5 as a function of bias offset.

charge. Due to the observation of dispersive electron transport, yet nondispersive hole transport,[12] it is proposed that mobile holes recombine with trapped electrons. As the external device current is zero 20 μs after voltage turnoff, the one-dimensional drift-diffusion equation $J = e\mu_{\text{drift}} pE - kT\mu_{\text{diffusion}}\, dp/dx$ can be solved numerically for the hole density p using the Poisson equation $dE/dx = (e/\varepsilon)p$, where e is the electronic charge, μ_{drift} and $\mu_{\text{diffusion}}$ are the drift and diffusion mobilities, respectively, p is the hole density, E the applied electric field, k the Boltzmann constant, T the temperature, and ε the dielectric constant. It is straightforward to show by numerical integration that for arbitrary anodic fields and hole surface densities the integrated hole density in the device is related to the applied bias by

$$p(V) \propto \exp\left(\frac{e}{kT} \frac{\mu_{\text{drift}}}{\mu_{\text{diffusion}}} V \right).$$

Assuming a Langevin-type recombination process,[1] the delayed EL intensity should simply be proportional to the product of the trapped electron concentration and hole density, which depends exponentially on the bias offset. As there is evidently a constant contribution to the delayed EL which is bias offset independent and most probably arises from geminately bound carrier pairs, the peak data in the inset of Fig. 5 are differentiated with respect to the bias. The result is shown in Fig. 6. Both host peaks exhibit an identical exponential dependence on the bias offset with an exponent of $0.08e/kT$. In most discussions of organic LED's the mobility of diffusion has been assumed to be equal to the drift mobility due to Einstein's law $eD = \mu kT$, where D is the diffusivity and μ is the carrier mobility. However, Monte Carlo simulations have shown that under conditions of strong disorder deviations from Einstein's law may occur, resulting in $\mu_{\text{drift}} < \mu_{\text{diffusion}}$.[13,14] This has also been used to explain the broadening of the tails of photocurrent transients.[14] There is currently an ongoing debate over the validity of Einstein's law in disordered semiconductors,[15,16] and the present results provide a straightforward approach to testing it. It appears that under fields of 10^5 V/cm the diffusion mobility is up to a factor of 12 greater than the drift mobility. This factor is in the same range as those previously reported for fields of 10^5 V/cm based on both simulations and indirect measurements of photocurrent-tail broadening.[13,14] The different offsets along the bias axis of the straight lines in Fig. 6 arise due

to the fact that electrons are trapped on either sites that emit in the blue or sites that emit in the green. Evidently, the concentration of electron traps on polymer sites corresponding to green emission is higher than the concentration on polyfluorene sites leading to blue emission. We note that this observation is incompatible with the notion of excimers leading to the broad redshifted feature, as excimer traps should exhibit identical dynamics to backbone traps.

In view of these conclusions, the observations in Figs. 2 and 4 can be interpreted as follows. Two trapping sites exist within the polymer, whereby structural defects on the backbone act as shallow electron traps and fluorenone defects[6] act as deep traps. The fact that a bias-offset-independent contribution is observed in the delayed emission suggests that there are also long-lived tightly bound geminate pairs (GP's) of carriers present, which may recombine radiatively. Such GP's have been observed in photoluminescence quenching experiments and have been shown to have lifetimes of over 100 μs at room temperature.[17] Shortly after turnoff the remaining free electrons are either trapped in deep sites or recombine with mobile holes in polyfluorene sites, resulting in an effective decrease of the green to blue emission ratio with respect to cw operation. As the delay is increased and the device is depleted of mobile carriers, recombination of geminately bound carrier pairs occurs initially on polyfluorene units. The lifetime of GP's increases with increasing degree of carrier localization, so that GP's formed with carriers trapped on fluorenone units are longer lived. Also, it has been shown that the lifetime of GP's decreases with increasing temperature,[17] so that in the time window studied the green emission contribution in Fig. 4 increases with respect to the blue-delayed emission as the temperature is raised. Furthermore, as the temperature is raised, weakly trapped carriers on the polyfluorene units become more mobile, thus increasing the probability of falling into a deep trap. As the spatial correlation between carriers becomes shorter due to a reduction in Coulomb capture radius, recombination in deep trap states becomes even more probable at elevated temperatures.

Gated EL spectroscopy is an extremely sensitive tool and can be used to detect impurities in the range of parts per million, as demonstrated by the addition of PtOEP. It can be used to deconvolve some of the complicated dynamical charge transport processes occurring in LED's and the role of chemical defects on charge trapping. In particular, it is to the knowledge of the authors the most direct technique of investigating the unique properties of nonequilibrium charge transport in highly anisotropic disordered polymeric semiconductors. The deviation from Einstein's law has been ignored in the development and description of organic electronic devices thus far. The technique presented should allow insights to be gained into the stochastic transport mechanisms of a whole variety of electronic materials and enables a detailed characterization of intrinsic and extrinsic trapping processes which affect both the cw emission and transient response. The clear observation of distinct trapping and delayed recombination processes giving rise to the blue and green spectral features seen in the cw luminescence demonstrates that excimers play little if no role in the solid-state emission properties of polyfluorenes. The present results complement our observations that the features in solution and film PL spectra of polyfluorene are actually identical, but merely display different weightings due to the dominance of three-dimensional exciton diffusion to traps in the solid state in comparison to one-dimensional on-chain diffusion in solution.[11]

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[1] D. J. Pinner *et al.*, Appl. Phys. Lett. **76**, 1137 (2000).
[2] V. Savvateev *et al.*, Adv. Mater. **11**, 319 (1999).
[3] P. W. M. Blom *et al.*, Phys. Rev. Lett. **80**, 3819 (1998).
[4] Y. V. Romanovskii *et al.*, Phys. Rev. Lett. **84**, 1027 (2000).
[5] P. A. Lane *et al.*, Phys. Rev. B **63**, 235206 (2001).
[6] E. J. W. List *et al.*, Adv. Mater. **14**, 374 (2002).
[7] J. I. Lee *et al.*, Chem. Mater. **11**, 1083 (1999).
[8] V. N. Bliznyuk *et al.*, Macromolecules **32**, 361 (1999).
[9] L. M. Herz *et al.*, Phys. Rev. B **61**, 13 691 (2000).
[10] M. A. Baldo *et al.*, Nature (London) **395**, 151 (1998).
[11] J. M. Lupton, M. R. Craig, and E. W. Meijer (unpublished).
[12] M. Redecker *et al.*, Appl. Phys. Lett. **73**, 1565 (1998).
[13] R. Richert *et al.*, Phys. Rev. Lett. **63**, 547 (1989).
[14] P. M. Borsenberger *et al.*, J. Chem. Phys. **94**, 8276 (1991).
[15] S. D. Baranovskii *et al.*, J. Non-Cryst. Solids **227-230**, 158 (1998).
[16] Y. A. Berlin *et al.*, Chem. Phys. Lett. **305**, 123 (1999).
[17] Yu. V. Romanovskii *et al.*, Phys. Rev. B **64**, 033104 (2001).